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Phase transition of $SrTiO_3$–$PbZrO_3$ solid solutions

E.P. Smirnova[a], A.V. Sotnikov[a,b,*], M. Weihnacht[b], W. Häßler[b],
V.V. Lemanov[a]

[a]*A.F. Ioffe Physical-Technical Institute, 194021 St. Petersburg, Russia*
[b]*Institute for Solid State and Materials Research, D-01171, Dresden, Germany*

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Abstract

Dielectric properties of $(1-x)$ $SrTiO_3-x$ $PbZrO_3$ ($0.5 \leqslant x \leqslant 1$) ceramic solid solutions were studied at frequencies between 10 and 10^5 Hz in a wide temperature range. Polarization loop measurements were used to identify antiferroelectric (AFE) and ferroelectric (FE) states. A crossover from the antiferroelectric to the relaxor ferroelectric state was observed. The dielectric relaxation spectra were found to be very broad without any peaks . The results can be understood in terms of possible AFE–FE phase frustration and local random fields, induced by a random distribution of the ions of different size and polarizability. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Perovskites; Powders: solid state reactions; Relaxation

1. Introduction

Since the discovery of antiferroelectricity in $PbZrO_3$ the studies of $PbZrO_3$-based solid solutions have been a topic of much interest. A characteristic feature of the solid solutions is that their phase diagrams have ferroelectric (FE) rhombohedral-tetragonal morphotropic phase boundary (FE_R–FE_T) and antiferroelectric (AFE)–FE phase boundary.[1–3] Compositions close to FE_R–FE_T and AFE–FE phase boundaries show excellent dielectric and electromechanical properties[4,5] which are very promising for ultrasonic transducers and large displacement actuators.[5–7] A fundamental study is essential for understanding of the origin and specific features of AFE–FE phase transitions. Many works have already been published concerning the $PbZrO_3$ family with various substitutions.[1–4] Some effects of Sr^{2+} and Ti^{4+} ions have been examined too. The phase diagram of the quarternary system $SrTiO_3$–$PbTiO_3$–$PbZrO_3$–$SrZrO_3$ at room temperature has been determined using X-ray diffraction measurements.[8] Dielectric measurements[8] were performed only at a fixed frequency of 550 kHz. Besides, polarization behavior of Sr-containing $PbZrO_3$–$PbTiO_3$ near the AFE–FE phase boundary has been studied only at room temperature.[8,9] Some of the $(1-x)$ $SrTiO_3-x$ $PbZrO_3$ solid solutions ($x = 0.1$, 0.2, and 0.3) have been investigated within the scope of the quarternary (Pb, Sr)(Ti, Zr)O_3 system study, but the frequency dependence of dielectric properties for this system is beyond the interest of researchers up to now.

In the present work, we study the dielectric spectra in a relatively wide frequency range and their temperature dependence for $(1-x)$ $SrTiO_3-x$ $PbZrO_3$ ($0.5 \leqslant x \leqslant 1$) solid solutions with special attention to the AFE–FE phase boundary. Temperature dependence of the induced polarization is also measured in order to identify the phase boundary.

2. Experimental procedure

Ceramic samples of $(1-x)$ $SrTiO_3-x$ $PbZrO_3$ with $x = 1$, 0.9, 0.8, 0.7, 0.6, 0.5 were prepared by a conventional ceramic procedure. The synthesis process was carried out in a lead oxide atmosphere in order to prevent lead losses. X-ray diffraction patterns showed that at room temperature all the samples were of single phase perovskite structure. Dielectric studies (both of real ε' and imaginary ε'' parts) were performed with a Solartron SI 1260 impedance/gain phase analyzer in the

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[*] Corresponding author. Tel.: +49-351-4659353; fax: +49-351-4659440.
E-mail address: a.sotnikov@ifw-dresden.de (A.V. Sotnikov).

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frequency range of 10 Hz–100 kHz at temperatures from−220 to 300°C. The a.c. measurement electric field amplitude was as low as 1 V/cm. The samples for measurements were disks of 8 mm in diameter and about 0.5 mm thick with burnt silver electrodes. The current integration method in the frequency range from 5 to 80 Hz was used to measure the polarization behavior of samples.

3. Results and discussion

The measurements confirm the well known fact that dielectric constant of lead zirconate does not show any frequency dispersion in paraelectric and antiferroelectric phases.[10] A weak dielectric dispersion appears in the vicinity of the phase transition temperature at $x=0.9$ and increases with x decreasing. Noticeable dispersion is observed in 0.7 $PbZrO_3$–0.3 $SrTiO_3$ (Fig. 1) and becomes remarkable for compositions with x up to 0.5. The observed dielectric anomalies are diffused and spread over a wide temperature range, more than 200°C. These results show a typical relaxor-like behavior: shifting of both ε' and ε'' peaks towards the higher temperatures with increasing frequency (Fig. 2). It was found that the frequency dependence of the permittivity maximum temperature T_m does not obey the Arrhenius law. This dependence was fitted with the Vögel–Fulcher relation

$$\tau = \tau_o \exp\left[U/k\left(T_m - T_f\right)\right], \qquad (1)$$

where τ_o is the inverse attempt frequency, U the activation energy, T_f the so called freezing temperature, and T_m the temperature of the ε'' peak.[11] For example, the obtained values of parameters for 0.5 $SrTiO_3$-0.5 $PbZrO_3$ are: $\tau_o=3.3\ 10^{11}$ s, $U=0.043$ eV, $T_{f=}115$ K. Close values of τ_o have been reported for the $PbIn_{1/2}Nb_{1/2}O_3$ (PIN) relaxor: $\tau_o=3\ 10^{11}$ s, $U=0.118$ eV.[12] The measured ε'' spectra in (1–x) $SrTiO_3$–x $PbZrO_3$ for compositions with $0.5 \leqslant x \leqslant 0.7$ were found to show neither peaks nor shrinkage in the measured frequency range in contrast to the ε'' spectra for PIN in the same

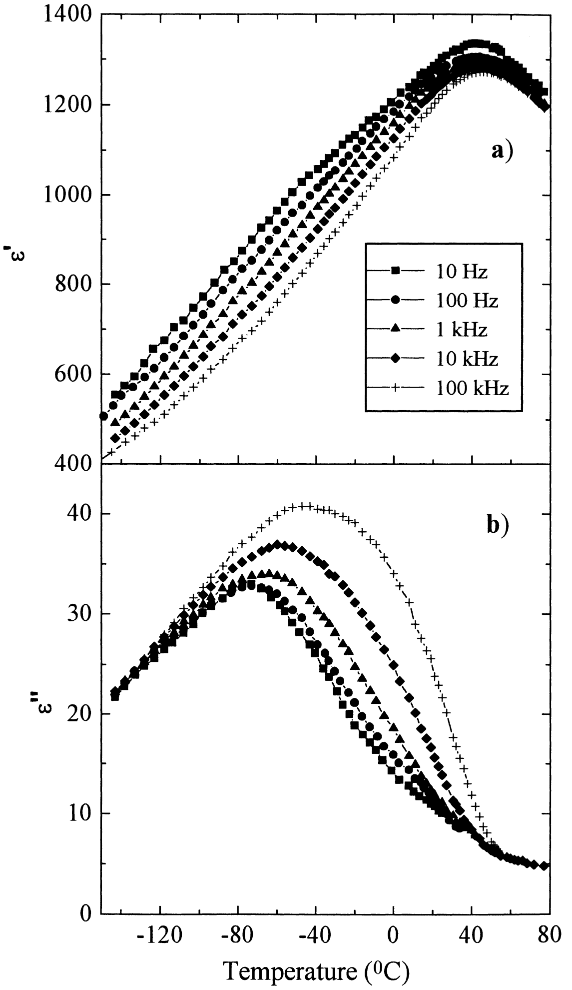

Fig. 1. Temperature dependence of the real (a) and imaginary (b) parts of the dielectric constant for the 0.3 $SrTiO_3$–0.7 $PbZrO_3$ ceramic sample at various frequencies.

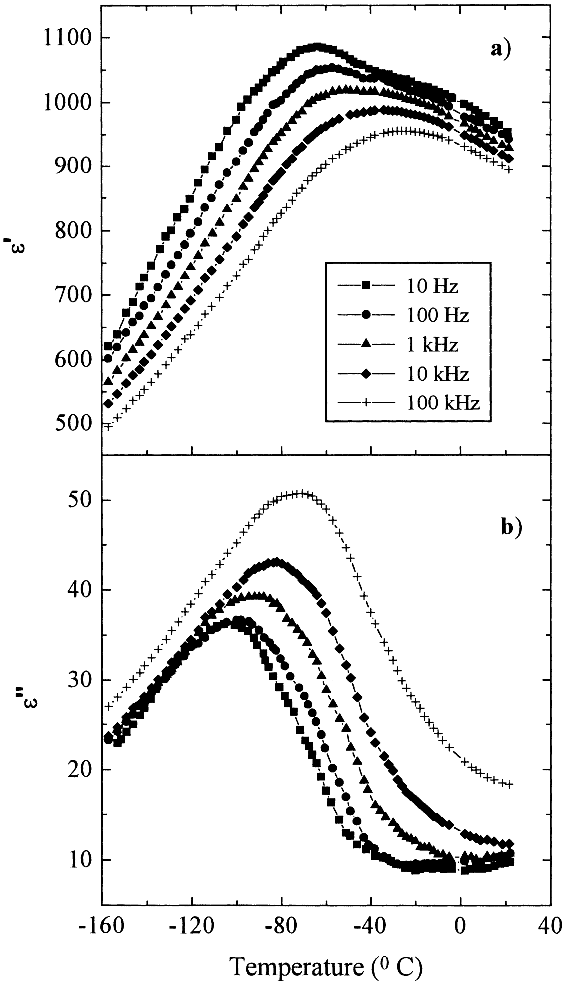

Fig. 2. Temperature dependence of the real (a) and imaginary (b) parts of the dielectric constant for the 0.4$SrTiO_3$–0.6$PbZrO_3$ solid solution at various frequencies.

frequency range (Fig. 3). On the other hand, the spectra are quite similar to ones observed in PLZT at frequencies up to 10^6 Hz.[13,14] Probably, ε'' vs frequency dependences for $SrTiO_3$–$PbZrO_3$ have peaks only at higher frequencies (10^8–10^{10} Hz) as it is the case for PLZT. Obviously, as for classical relaxors, such a behavior implies the absence of a unique relaxation time; rather there exists a broad distribution of relaxation times.[11–14] Usually, such spectra are described by a well-known approximate expression:[11]

$$\varepsilon''(\omega, T) \cong (\pi/2)\varepsilon_0(T)g(1/\omega, T), \qquad (2)$$

where $g(1/\omega, T)$ is the distribution of relaxation times and $\varepsilon_0(T)$ the low-frequency limit of $\varepsilon'(T, \omega)$.

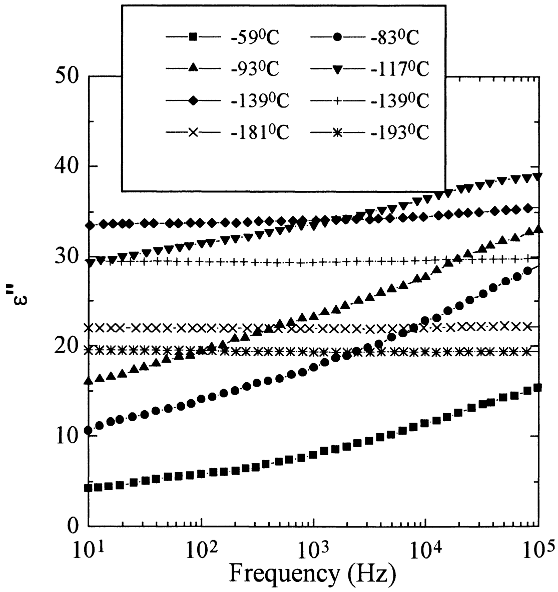

Fig. 3. Imaginary part of the dielectric constant as a function of frequency for the 0.5 $SrTiO_3$–0.5 $PbZrO_3$ ceramics at different temperatures.

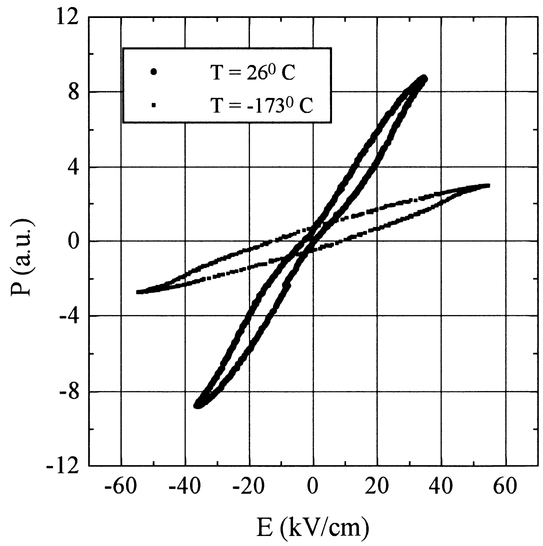

Fig. 4. Hystersis loops of the 0.3 $SrTiO_3$–0.7 $PbZrO_3$ ceramics at $T = 26°C$ and $T = -173°C$.

The polarization study was used to clarify the phase transition character and to locate the AFE–FE phase boundary. Compositions with $x = 0.9$ and 0.8 have a linear field dependence of polarization in the field range of 0–50 kV/cm and double hysteresis loops at the field value of 60 kV/cm observed at the temperature close to the phase transition point. This obviously manifests a presence of the AFE phase. The solid solutions with $x = 0.5$ and 0.6 show a polarization behavior typical to the ferroelectric phase in the whole temperature range. These data are in agreement with the results of Refs. 8 and 9. Lead zirconate with 0.3 $SrTiO_3$ is commonly supposed to be a ferroelectric,[8,9] but we have found double hysteresis loops at room temperature that manifest the AFE state while at $-173°C$ conventional FE hysteresis loops have been observed, that tells about the FE state (Fig. 4). Such a behavior of polarization allows us to assume that AFE–FE phase boundary has to be located close to the concentration $x = 0.3$ and the boundary is not a vertical line (Fig. 5).

On the base of the above results the antiferroelectric-to-relaxor crossover and the dielectric relaxation of the system can be understood as follows. The AFE clusters dominate in 0.3 $SrTiO_3$–0.7 $PbZrO_3$ at room temperature, but with temperature decreasing, the FE clusters become dominant. A coexistence of the AFE- and the FE-states leads to AFE–FE phase frustration accompanied by a strong dielectric relaxation. At low temperatures, the FE clusters spread over the whole sample

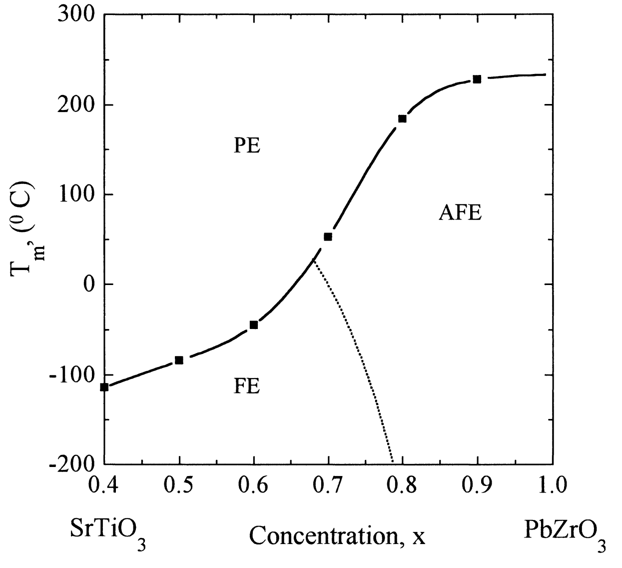

Fig. 5. Phase diagram of $(1{-}x)SrTiO_3$–$x\,PbZrO_3$ system ($0.5 \leqslant x \leqslant 1$) deduced from dielectric (symbols) and hysteresis loop measurements. The dashed line corresponds to assumed position of AFE–FE phase boundary. The solid line is a guide to the eyes.

and the FE state is formed. We assume that this frustration effect is of the same nature as proposed for $Rb_{1-x}(NH_4)_xH_2PO_4$ mixed crystals as well as for spin glasses (see Refs. 11 and 15 and references therein).

As for the very strong dielectric relaxation in the FE phase far from the AFE–FE boundary, it can be connected with random fields due to difference in ionic size and polarizability and compositional imhogeinity of the solid solutions. A presence of random fields and their effect on polar clusters are often considered as a reason of the relaxor behavior.[16]

Acknowledgements

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